

REMARKS

Claims 2, 13-15 and 31 are canceled. Claims 1, 3-12, 16-30 and 32-34 and new Claims 35-38 remain active in the case. Reconsideration is respectfully requested.

Claim Amendments

Claim 1 has been amended by incorporating the limitation of Claim 2 therein, which latter claim has now been canceled.

Claim 7 has been amended to recite that after the manganese oxide ore has been reduced, it is cooled while under a non-oxidizing atmosphere as supported by the disclosure at page 22, first full paragraph.

New Claims 35-38 are supported by the disclosure of the first paragraph on page 13 of the text of the specification. Entry of the amendments to the claims is respectfully requested.

Claim Rejection, 35 USC 112, First Paragraph

As to the matter of the alleged lack of support for the limitation in Claim 9 regarding the iron dissolution degree in sulfuric acid, applicants note that this precise limitation is the subject matter of original Claim 2, which limitation is also disclosed at in the second paragraph on page 14 of the text. Withdrawal of the new matter rejection is respectfully requested.

As to the matter of the term "necessary period to produce said manganese dioxide," the same has been eliminated from the Claim 9. Accordingly, the first paragraph rejection is believed obviated and withdrawal of the same is respectfully requested.

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Claim Rejection, 35 USC 112, Second Paragraph

The issue raised with respect to Claim 9 is obviated by the amendment made to the claim as noted above concerning the first paragraph rejection. The claim simply recites that the product has the indicated iron dissolution degree. Withdrawal of the rejection is respectfully requested.

Invention

As now stated in Claim 1, the invention is directed to a treated manganese dioxide ore that is useful for producing manganese sulfate. The treated ore of the invention has a degree of manganese dissolution of 98.0 % by weight or higher based on the manganese contained in the treated manganese dioxide ore when dissolved in sulfuric acid and having a degree of manganese dissolution of 70 % by weight or higher based on the iron contained in the treated manganese dioxide ore when dissolved in sulfuric acid.

The present invention relates to a treated manganese ore from which manganese sulfate is derived by which electrolytic grade manganese dioxide is prepared. The treated manganese ore is of exceptional purity, as stated in Claim 1, having a degree of manganese dissolution of 98.0 % or higher based on the manganese content of the treated ore. The process by which the treated ore of the invention has the advantages of reducing the amount of slag in the production step and also reduces the potassium content of the ore which is important in preparing a product which can be used to prepare manganese dioxide of high purity for use in electrolytic applications.

Claim 7 is directed to the aspect of the invention by which the treated manganese ore of

the invention is prepared by subjecting an appropriate manganese ore to reduction by contact with at least one reducing gas of methane, carbon monoxide and hydrogen in combination with a diluent of an inert gas. The amount of the reducing gas used ranges from 1.0 to 2.0 times the theoretical amount necessary to reduce the manganese ore.

Another embodiment of the process is that following the reduction treatment of the ore, the reduced ore is immersed in water having a temperature of 70° C to the boiling point at atmospheric pressure as embodied in Claim 10.

Prior Art Rejection

Claims 1-4, 6, 7-9 and 16-21 stand rejected based on 35 USC 103(a) as obvious over Yagihashi et al. This ground of rejection is respectfully traversed.

Claims 1-9 and 16-22 stand rejected based on 35 USC 103(a) as obvious over Welsh, U. S. Patent 3,375,097. This ground of rejection is respectfully traversed.

Applicants note that both the Yagihashi et al and Welsh references disclose the reduction of manganese ore with a reducing gas at a temperature of 700° C. However, as shown in Figure 6 on page 18 (1062) of Yagihashi et al, after MnO₂ has been reduced to MnO, when air is blown over the MnO after it has been cooled to room temperature, the MnO oxidizes again. That is, it reoxidizes. Upon reoxidation, it is believed Mn₃O₄ is produced which can be indicated as the combination: MnO₂·2MnO. Because the MnO₂ component of the combination is insoluble in acid, the degree of manganese dissolution in an acid is diminished. Thus, the degree of reoxidation resistance is an important factor in determining the degree of dissolution of treated (reduced) manganese ore in an acid. With respect to Yagihashi et al the reoxidation ratio can be

read off from the graphs of Figure 6. That is, the reoxidation ratio can be determined from the expression: (maximum reduction in weight-(reduction in weight after introduction of air))/maximum reduction in weight x 100. The percentage reduction from the graphs of Figure 6 can be estimated to be 3.8 %. This means that with respect to the reduced ore obtained by the means described in Yagihashi et al, the degree of dissolution of the reduced ore in acid is 100-3.8 or 96.2 %. This degree of manganese dissolution is not satisfactory.

In the work leading to the present invention, applicants have taken particular note of Fe in the manganese ore. That is, a key aspect of the present invention is that applicants have succeeded in reducing Fe in the ore into metallic Fe, as well as reducing manganese oxide. Applicants have found that the metallic iron that is produced functions as an antioxidant to MnO. In the present process, because the reoxidation of MnO is prevented by the metallic Fe, That is, in the event the MnO is exposed to oxygen in the air, the metallic Fe prevents reoxidation of the MnO. This prevention or suppression of reoxidation is also exhibited when the MnO is subjected to the oxygen that is present in aqueous solutions when the MnO is leached and dissolved into solution. According to the present invention, the degree of dissolution in acid of manganese is 98 % by weight or higher. Applicants at this point note that Claim 1 has been amended to recite both the degree of manganese dissolution and the degree of iron dissolution in sulfuric acid solution which characterize the treated product of this invention.

It is important to note at this point that the manner in which Yagihashi et al handle the presence of iron in the processing described is quite different from the manner in which the presence of iron is handled in the present invention. That is, Yagihashi et al describes on page 1063, left column, lines 18 to 23 that the reduced iron that is formed at low temperature is a

cause of the carbon deposition that is noted when carbon monoxide is used as the reducing gas. On page 1064, right column, lines 3 to 16 the reference states that because the occurrence of the deposition of carbon is undesirable for various reasons, conditions must be selected to avoid the carbon deposition, and these include the type of ore selected, the high temperature chosen for reduction and the use of a low CO concentration. Clearly, the view of Yagihashi et al is that the presence of Fe is something that does more harm than good. Further, Yagihashi et al sets the conditions by which no Fe is formed. That is, in order to improve the oxidation resistance of the MnO that is prepared, Yagihashi et al employ the technique of increasing the crystallinity of the MnO product. This objective is quite different from the means by which oxidation resistance is achieved in the present invention.

As to the Welsh patent, the form in which iron is present in the ore of the reference is Fe₂O₃ as described at column 14, line 50. The Fe₂O₃ is not reduced to Fe in the process of the reference. Accordingly, the technique for improving the oxidation resistance of MnO in Welsh is quite different from the procedure of the present invention. It is believed that in the case of Welsh, improvement in oxidation resistance is achieved by the growth of crystals of MnO at a central point in the apparatus employed in the batch process disclosed in the patent. The patent discloses that after an apparatus is filled with an ore, an air-methane gas is blown from the bottom of the apparatus up-through a bed of the ore. Heat and reducing gas (CO and H₂) are supplied to the unit by partial combustion of the methane gas, and the ore positioned in the central region of the apparatus is reduced at 1000 to 2000° F (preferably 1300 to 1400°F). That is, 538 to 1093° C (preferably 704 to 760° C). Welsh discloses in column 13, line 6 from the bottom of the patent that it takes 20 hours to achieve a steady state in the operation disclosed.

The process requires a long period of time to elevate the temperature in the process and a long time to cool the ore to end the process. The overall operation requires about 50 hours (column 15, line 10) Under these conditions applicants believe that MnO crystals form in the central part of the apparatus, as the crystals form over the long period of time. However, it must be noted that the method of stabilizing MnO in the patent gives rise to a significant problem in that the product obtained contains alkali metal, particularly potassium. The presence of this element adversely affects the properties of batteries prepared from the reduced manganese ore. Accordingly, in conventional processing, potassium is eliminated from the ore at the "jarosite formation step" after the ore is dissolved. However, in the process of the present invention, the potassium elimination ratio demanded is not only achieved by the jarosite formation step.

It is known in the art that in order to achieve a satisfactory K elimination ratio, it is necessary to conduct operations of K removal by direct elimination such as by leaching the ore in hot water or some such similar process. Sasaki achieves K elimination by leaching an ore under the relatively severe conditions of leaching in hot water of a temperature not lower than 100° C in an autoclave. However, in the case of the preparation of crystals of MnO of sufficient size, although the oxidation resistance of the MnO is improved, the leaching operation employed to remove potassium becomes more difficult. That is, as the particle size of the MnO crystals increases, because the specific surface area of the crystals decreases and the degree of contact of the liquid leaching agent becomes small, it becomes difficult to eliminate soluble substances from the crystals of MnO. On the other hand, in the present invention, because of the presence of iron in the MnO as a result of the reduction of Mn ore in a relatively short time, the growth of MnO is suppressed which means that the surface area of the MnO produced is kept large. The

elimination of K by leaching is thus made relatively easy. The present invention is the selection of appropriate conditions for the reduction of manganese ore by which metallic Fe is produced and crystal growth of MnO is suppressed. These conditions include the selection of a type of Mn ore and process conditions including thermal history and the type of reducing gas. That is, a MnO₂ ore is chosen that contains Fe, has a comparatively high Mn purity and is reduced rapidly at 20 to 120 min/degree in a reducing gas atmosphere that contains no oxygen at a temperature of 400 to 790° C to attain a degree of iron dissolution of 70 % or more. K can be easily eliminated by leaching from such a product since it contains metallic Fe that prevents reoxidation of the MnO. On the other hand, the MnO products produced by processes of Yagihashi and Welsh are easily oxidized, and because of this fact, the degree of MnO dissolution of 98% by weight or higher as in the present invention can not be achieved. Accordingly, the product and process embodiments of the present invention are not suggested by the two references and withdrawal of the obviousness grounds of rejection is respectfully requested.

Claims 1-6 stand rejected based on 35 USC 103(a) as obvious over Kane et al. This ground of rejection is respectfully traversed.

The Kane et al disclosure describes a substantially different method of processing an ore than that of the present invention. That is, in Kane et al, manganese nodules are subjected to SO₂ gas, which is the only type of reducing gas described in the reference, and not any of the hydrogen, methane or CO gaseous reducing agents of the present method claim embodiments. This is significant because in the process of the reference a reduced MnO ore is not obtained, but rather the SO₂ treatment, with respect to manganese, results in the simultaneous reduction of manganese oxide in the ore to divalent manganese and formation of Mn(II) sulfate. An aqueous

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manganese sulfate solution is thus obtained by an aqueous, slightly acid leach. Clearly, the product of present Claim 1 is neither shown or suggested. Withdrawal of the rejection is respectfully requested.

Claims 1-6 stand rejected based on 35 USC 103(a) as obvious over El Tawil, U. S. Patent 4,985,216. This ground of rejection is respectfully traversed.

As stated on the record previously, the El Tawil patent discloses a process for treating a Mn-Ag ore for the recovery of silver values from the ore. (See, for example, Claim 1 and column 5, lines 40-42.) In the first step of the process the ore is subjected to roasting in the presence of one of the hydrocarbon reducing gases disclosed therein to reduce the MnO₂ content to the desired level and then silver is recovered by hydrometallurgical techniques (col 3, lines 1-12). However, El Tawil in column 4 discloses very little as to the nature and composition of the reduced Mn ore obtained. It is noted that in column 4, lines 17 and 18, cooling of the treated ore material occurs with an aqueous bath. This is quite different from the cooling technique of the present invention which occurs in a non-oxidizing atmosphere as claimed in present Claims 7 and 24. There is absolutely no teaching or suggestion of a reduced ore as set forth in present Claim 1 which **must** have a degree of manganese dissolution in sulfuric acid of 98.0 % or more and simultaneously a degree of iron dissolution of 70 % by weight or greater in sulfuric acid. Furthermore, it can not be said that just because the patent discloses a process of reducing an ore with a simple alkane, that does **not** include the methane reducing agent of the present claims, a reduced manganese ore is produced that inherently is the same product as that now claimed in the present invention.. As shown in detail above, in order to prepare the reduced ore of the invention, special process aspects must be followed if a product within the scope of the invention

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is to be obtained. El Tawil contains no disclosure of the factors which produce the product of the present invention. Accordingly, the present product is not shown or suggested by the reference and withdrawal of the rejection is respectfully requested.

As disclosed in column 4, lines 19-37, the reduced ore is first subjected to leaching with the likes of sulfuric acid to remove manganese values therefrom. Apparently thereafter by some means the manganese oxide which is obtained is treated to form a manganese sulfate solution in turn to make an electrolytic grade manganese dioxide. Thus, the route employed by the patent to prepare a grade of manganese oxide acceptable from which to obtain an electrolytic grade of MnO₂ is quite different from the method of production of the process claim embodiments of the present invention. Further contrary to the remarks by the Examiner at page 8, lines 13-15, El Tawil does not simply teach the treatment of a manganese ore with a reducing gas to prepare a grade of manganese oxide which in and of itself is acceptable as a material from which to prepare electrolytic grade manganese dioxide. Withdrawal of the reference is respectfully requested.

Claims 32-34 stand rejected based on 35 USC 103(a) as obvious over El Tawil, U. S. Patent 4,985,216, Kane et al, U.S. Patent 3,810,827 or Welsh or Yagihashi et al in view of Bowerman et al, U.S. Patent 4,489,043, Takehara, U. S. Patent 5,746,902, Andersen et al, U.S. Patent 6,214,198, Andersen et al, U.S. Patent 4,948,484 or Riggs, U.S. Patent 4,477,320. This ground of rejection is respectfully traversed.

As stated on the record above, none of the El Tawil, Kane et al, Yagihashi et al or Welsh patents shows or suggests a treated manganese ore which has the specific sulfuric acid dissolvability requirement of the present claims as it pertains to dissolution os Fe and Mn. Yet,

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the distinctly different product of the present invention, as discussed above, provides important advantages when for the preparation of an electrolytic manganese dioxide material because of the very high dissolvability of manganese and because of the ready removal of potassium from the present product. Moreover, although the Bowerman et al, Takehara, Andersen et al, Andersen et al, and Riggs patents disclose the electrolytic oxidation of manganese sulfate to electrolytic grade manganese oxide, the amount of slag generated in these processes can not be reduced to the low levels achieved in the present invention which uses the claimed treated manganese ore of the invention. Further, the prior art processes do not result in the reduced concentration levels of potassium impurity in the desired manganese dioxide product in comparison to the reduced potassium levels achieved in the present invention as seen above.

As pointed out above, it is believed that the Examiner errs when he states that the primary patents, particularly Welsh and Yagihashi et al teach or suggest the presently claimed product and the process embodiments of producing a treated manganese ore. Thus, a process of producing an electrolytic grade manganese dioxide would not be obvious in view of the art which does not teach or suggest the treated manganese dioxide of Claim 1, nor the process of preparing a treated manganese ore of Claim 7. Accordingly, the stated ground of rejection is believed obviated and withdrawal of the rejection is respectfully requested.

Claim 34 stands rejected based on 35 USC 103(a) as obvious over Takehara, U. S. Patent 5,746,902 or Andersen et al, U.S. Patent 6,214,198 or Riggs, U.S. Patent 4,477,320. This ground of rejection is respectfully traversed.

With respect to Claim 34, the claimed electrolytic manganese dioxide is, in fact, dependent on the reduced ore or reduced treated ore of Claim 1 or 5. This product has a very

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high degree of sulfuric acid dissolution of 98 % by wt or higher and even 99 % by wt or higher. Accordingly, when a manganese dioxide prepared by the process of the invention is employed in the process steps of Claim 34, the amount of slag which is generated can be reduced by a factor of 1/3 to 1/4 which reduces the load on the environment and reduces the concentration of potassium impurity in the electrolytic product manganese dioxide. This fact is shown in Table 1 of the specification where 6 examples within the scope of the invention of treated manganese ore have much lower potassium contents than the treated ores of Comp. Exs. 2 and 3, which examples do not conform to the limitations of the present process claims. On the other hand, none of the cited and applied patents teach the treated manganese oxide material of the present claims as described above and therefore they could not possibly and do not suggest the claimed electrolytic grade manganese dioxide of present Claim 34. Accordingly, the rejection based on the cited and applied patents is believed overcome and withdrawal of the same is respectfully requested.

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It is now believed that the application is in proper condition for allowance. Early notice to this effect is earnestly solicited.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,
MAIER & NEUSTADT, P.C.



Norman F. Oblon
Attorney of Record
Registration No.: 24,618

Frederick D. Vastine, Ph.D.
Registration No.: 27,013



22850

TEL: 703-413-3000
FAX: 703-413-2220